Short communication

Development of PVA based micro-porous polymer electrolyte by a novel preferential polymer dissolution process

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Abstract

A micro-porous polymer electrolyte based on PVA was obtained from PVA–PVC based polymer blend film by a novel preferential polymer dissolution technique. The ionic conductivity of micro-porous polymer electrolyte increases with increase in the removal of PVC content. Finally, the effect of variation of lithium salt concentration is studied for micro-porous polymer electrolyte of high ionic conductivity composition. The ionic conductivity of the micro-porous polymer electrolyte is measured in the temperature range of 301–351 K. It is observed that a 2 M LiClO$_4$ solution of micro-porous polymer electrolyte has high ionic conductivity of 1.5055×10^{-3} S cm^{-1} at ambient temperature. Complexation and surface morphology of the micro-porous polymer electrolytes are studied by X-ray diffraction and SEM analysis. TG/DTA analysis informs that the micro-porous polymer electrolyte is thermally stable upto 277.9 °C. Chronoamperommetry and linear sweep voltammetry studies were made to find out lithium transference number and stability of micro-porous polymer electrolyte membrane, respectively. Cyclic voltammetry study was performed for carbon/micro-porous polymer electrolyte/LiMn$_2$O$_4$ cell to reveal the compatibility and electrochemical stability between electrode materials.
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1. Introduction

The recent developments in the field of ionic conducting polymer electrolytes, which could be utilized for rechargeable lithium batteries, have been widely investigated [1–4]. Generally, gel polymer electrolytes are prepared by incorporating liquid electrolytes into a matrix polymer such as polyacrylonitrile (PAN), poly(vinylidene fluoride) (PVdF), poly(vinyl chloride) (PVC), poly(vinyl pyrrolidone) (PVP) and poly(vinyl sulfone) (PVS) [5–8]. These polymer electrolytes exhibited ionic conductivity of 10^{-3} S cm^{-1}, but they do not have mechanical properties sufficient to produce thin films. Hence, poly(vinyl alcohol) (PVA) is chosen in place of the above-mentioned polymers, which exhibited high abrasion resistance, elongation, tensile strength and flexibility. Rajendran et al. [9] reported that the gel polymer electrolyte based on PVA has ionic conductivity of about 1.2886×10^{-3} S cm^{-1}. Further ionic conductivity is improved by preferential polymer dissolution process followed by soaking in Li-salt electrolyte solution to get micro-porous polymer electrolyte. This procedure requires critical moisture control only during the last activation step and also micro-porous polymer electrolyte based on PVA has yet to be studied.

Hence, in the present work, the PVA based micro-porous polymer electrolyte was prepared and its complexation, morphology, thermal stability, ionic conductivity, electrochemical stability and cyclic voltammetry studies were also investigated.

2. Experimental

PVA (M_w: 1,46,000), PVC (M_w: 2,33,000) and LiClO$_4$ received from Aldrich, USA were dried at 100 °C in vac-

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uum oven under 10^{-3} Torr pressure for 48 h and EC and DEC received from Across Organic, Belgium were used without further purification for the preparation of polymer electrolyte. Appropriate quantities of PVA, PVC were dissolved in dimethyl formamide (DMF). The solution was stirred continuously for several hours until a homogeneous suspension was obtained. The homogeneous solution was poured on a glass plate to form a thin film of the required thickness using a Doctor blade. The film was then dried at 80 °C in a vacuum oven under 10^{-3} Torr pressure for 5 h to remove any further trace amount of DMF. The thickness of the formed films was in the range of 150–200 μm. The above prepared cast polymer films were immersed in THF for the preferential dissolution of PVC to get micro-porous polymer membranes. The micro-porous polymer membranes were activated by soaking in 1 M LiClO$_4$ electrolyte solution of EC and DEC [1:1 (V/V) ratio] to get a micro-porous polymer electrolyte. Finally, the effect of various salt concentrations was carried out for micro-porous polymer membrane of high ionic conductivity system.

The XRD equipment used in this study is a JOEL-X-ray diffractometer using nickel filtered Cu Kα radiation at a scan rate of $10°$ min^{-1} to examine the crystallinity of the micro-porous polymer electrolyte.

The SEM equipment used in this study is a JSM-scanning electron microscope which was used to examine the surface morphology of micro-porous polymer membrane.

The TG/DTA equipment was used at a scanning rate of $10 °C$ min^{-1} to find the thermal stability of the micro-porous polymer electrolyte.

The ionic conductivity of the micro-porous polymer electrolyte was evaluated from a Cole-Cole impedance plot using an EG&G-electrochemical impedance analyzer in the frequency range of 10 Hz to 100 kHz with a signal amplitude of 10 mV by placing the micro-porous polymer electrolyte in between two stainless steel (SS) disc electrodes in a specially designed cell setup for conductivity studies.

The electrochemical stability of micro-porous polymer electrolyte was studied by linear sweep voltammetry (LSV). The cell set consists of SS as a working electrode, lithium as a counter and a reference electrode and micro-porous polymer electrolyte was kept in between the above electrodes at a scanning rate of 1 mV s^{-1}. The cell was assembled in a dry box under argon atmosphere. A dc polarization cell was constructed by sandwiching the micro-porous polymer electrolyte in between symmetrical lithium metal electrodes and the experiment was performed as described previously [10,11] to find the lithium transference number of the polymer electrolyte. Cyclic voltammetry was performed on a carbon/micro-porous polymer electrolyte/LiMn$_2$O$_4$ cell in the potential range of 3–5 V versus Li$^+$ at a scanning rate of 1 mV s^{-1} to find the reversibility and electrochemical stability of the polymer electrolyte.

3. Results and discussion

3.1. X-ray diffraction analysis

In order to investigate the influence of lithium salt concentrations on the micro-porous polymer membrane, XRD examinations were conducted by soaking the micro-porous polymer membrane in 1 M LiClO$_4$, 1.5 M LiClO$_4$, 2 M LiClO$_4$ and 2.5 M LiClO$_4$ electrolyte solutions. The XRD patterns of the PVA based micro-porous polymer membrane and the polymer membrane soaked in 2 M LiClO$_4$ and 2.5 M LiClO$_4$ electrolyte solutions are given in Fig. 1(a)–(c). The following observations were made from the XRD patterns:

1. The intensity of diffraction peaks decreases with increase in salt concentration up to 2 M LiClO$_4$. This shows a decrease in crystallinity of the micro-porous polymer electrolyte. It confirms the complete dissociation of LiClO$_4$ and also the uptake of the electrolyte solution by the micro-porous polymer membrane is somewhat higher than the solid polymer film as shown in Fig. 1(a and b).
2. The diffraction peak of PVA based micro-porous polymer membrane is displaced from $2\theta = 16.41°$ to $2\theta = 17.06°$, when the polymer membrane is soaked in Li-salt electrolyte solution. It confirms complex formation in between the polymer blend film and Li-salt.
3. In addition, further increase in salt concentration (2.5 M LiClO$_4$) increases the crystallinity nature of the polymer electrolyte, which may be due to the undissociation of LiClO$_4$ salt, which is evident from Fig. 1(c).

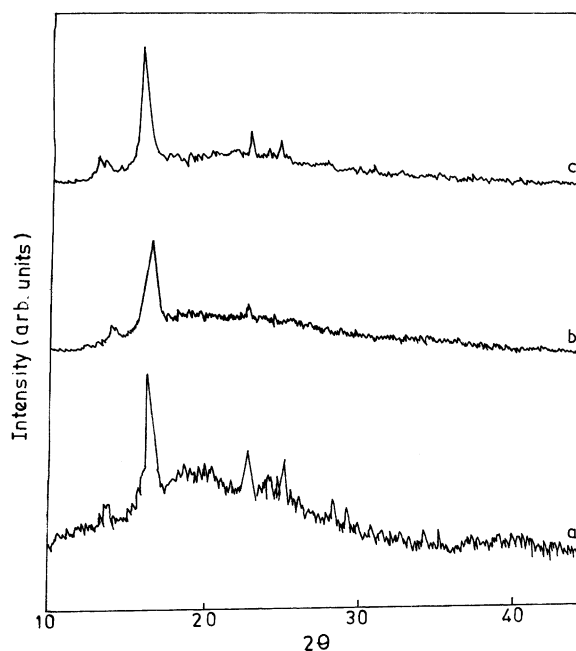Fig. 1. X-ray diffraction patterns for (a) micro-porous polymer film, (b) micro-porous polymer film soaked in 2 M LiClO$_4$ electrolyte solution and (c) micro-porous polymer film soaked in 2.5 M LiClO$_4$ electrolyte solution.

Thus, the X-ray diffraction studies reveal complex formation in the polymer matrices.

3.2. SEM analysis

Fig. 2(a and b) shows the SEM photographs of the micro-porous polymer membrane of high ionic conductivity system, before and after soaking in electrolyte solution. It can be seen from the photograph that the micro-porous structure increases with increase in removal of PVC content. Hence, the uptake of electrolyte solution by the micro-porous polymer membrane is higher than that of conventional polymer film. After soaking in electrolyte solution, the micro-porous membrane could not be observed with large voids and cavities of different sizes due to the formation of a complex process by the interaction of the plasticizer and the polymer chain which is evident from Fig. 2(b).

3.3. Thermal analysis

Fig. 3 shows TG and DTA curve of the PVA based micro-porous polymer electrolyte of high ionic conductivity system. It can be seen from the TG curve that the first decomposition of PVA occurs at 277.9 °C with a rapid weight loss of 51.0% which is closely related with the reported value [12]. It follows a complete decomposition of 85.6% upto 495.0 °C. This is due to decomposition of low molecular weight alka-
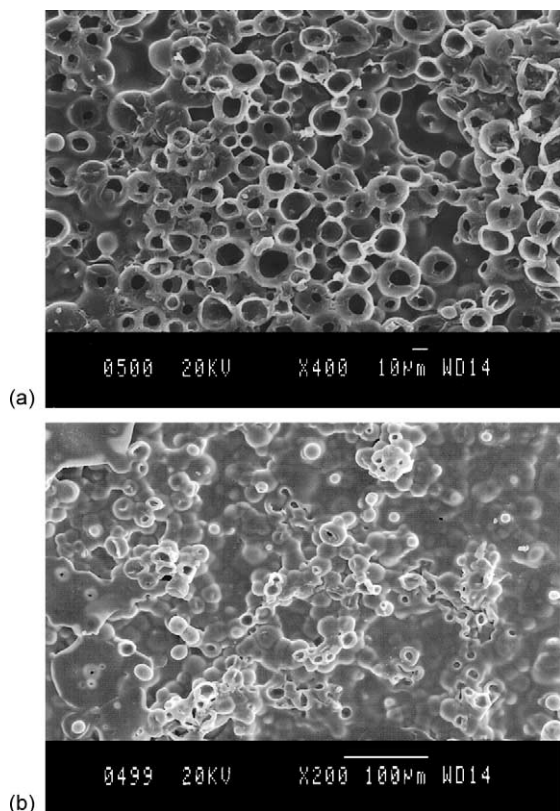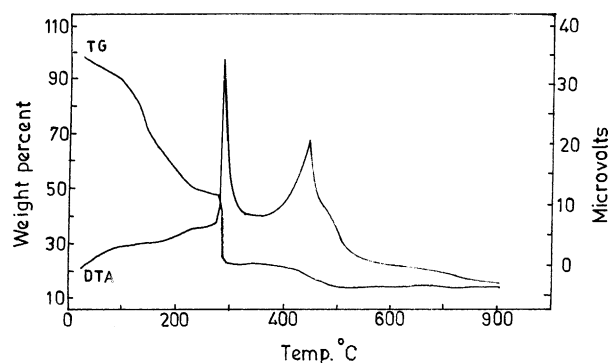

Fig. 3. TG/DTA curve for micro-porous polymer electrolyte.

nes, alkenes, aldehydes, ketones, etc., and also acetaldehyde and acetic acid in the case of pure PVA [13]. From the thermogram, it is found that there is a residue of about 14.4% and most of this could originate from the unhydrolysed acetate portion of PVA.

In the DTA curve, two large exothermic peaks are observed at 289.1 and 443.9 °C. The first decomposition occurs in the range of 271.5–321.9 °C and the second decomposition occurs in the range of 371.9–484.5 °C with an appreciable weight loss of about 85.1%. This indicates the complete decomposition of the polymer film, which is in good agreement with the observed TG curve. From the above discussion, it is concluded that the thermal stability limit of the micro-porous polymer electrolyte is 277.9 °C.

3.4. Conductivity studies

The ionic conductivity of PVA based polymer electrolyte and micro-porous polymer electrolyte are given in Table 1. It can be seen from the table that the micro-porous polymer electrolyte of composition 50:50 wt.% PVA–PVC based polymer blend film has a higher ionic conductivity of 0.5401×10^{-3} S cm^{-1} at room temperature than all other micro-porous polymer electrolytes besides the PVA based gel polymer electrolyte. This is due to higher uptake of electrolyte solution by the micro-porous polymer electrolyte. Finally, the effect of lithium salt concentrations was carried out for the micro-porous polymer electrolyte of high ionic conductivity system, because the ionic conductivity of the polymer electrolyte depends on the concentration of the ionic species and their mobility. The ionic conductivity of micro-porous polymer membrane of high ionic conductivity system

Fig. 2. SEM photographs for (a) PVA based micro-porous polymer membrane and (b) PVA based micro-porous polymer electrolyte.

Table 1
Conductivity data of micro-porous polymer electrolyte at room temperature

S. no.	PVA (%)	PVC (%)	Conductivity (S cm^{-1})
1	100	0	0.1625×10^{-3}
2	90	10	0.3232×10^{-3}
3	80	20	0.4097×10^{-3}
4	70	30	0.4566×10^{-3}
5	60	40	0.5070×10^{-3}
6	50	50	0.5401×10^{-3}

Table 2
Ionic conductivity values of micro-porous polymer membrane soaked in different concentrations of LiClO$_4$ electrolyte solution at various temperatures

Concentration	Ionic conductivity ($\times 10^{-3}$) (S cm^{-1})					
	301 K	311 K	321 K	331 K	341 K	351 K
1 M LiClO$_4$	0.5401	0.7293	0.8737	1.4539	2.1770	3.1416
1.5 M LiClO$_4$	0.8224	1.0188	1.9538	2.7515	3.6351	4.1783
2 M LiClO$_4$	1.5055	2.6676	3.4525	4.1728	5.6193	7.1552
2.5 M LiClO$_4$	1.2645	2.1349	2.9382	3.4471	4.9809	6.2944

soaked in different concentrations of LiClO$_4$ electrolyte solution was carried out in the temperature range of 301–351 K and are given in Table 2. For all the complexes, conductivity increases with increase in temperature as expected [14]. It seems to obey the VTF relation. The amorphous nature of the present polymer electrolyte facilitates the fast Li-ion motion in the polymer network and it further provides a higher free volume upon increasing the temperature [15]. The effect of addition of salt concentration in the polymer matrix on the logarithmic scale conductivity is shown in Fig. 4. It can be seen from the figure that the increase in conductivity is due to an increase in Li-salt concentration in electrolyte solution, which is due to the number of charge carriers in the polymer network. The micro-porous polymer electrolyte, consists of 2 M LiClO$_4$ complex, has high ionic conductivity of 1.5055×10^{-3} S cm^{-1} at room temperature. Beyond this concentration (2 M LiClO$_4$) the ionic conductivity decreases. This is due to the formation of ion pairs and ion triplet formation, which cause constraints of polymer segmental motion and also ionic mobility.

Typical plots of log conductivity versus inverse temperature (1000/T) for the micro-porous polymer electrolyte of the high ionic conductivity system in different salt concentrations are shown in Fig. 5. In general, on increase in temperature, the ionic conductivity increases due to the activation of internal modes and decreasing E_a values which reduce the crystalline nature of the polymer–salt complexes. The plots suggest that the non-linear ion transport in polymer
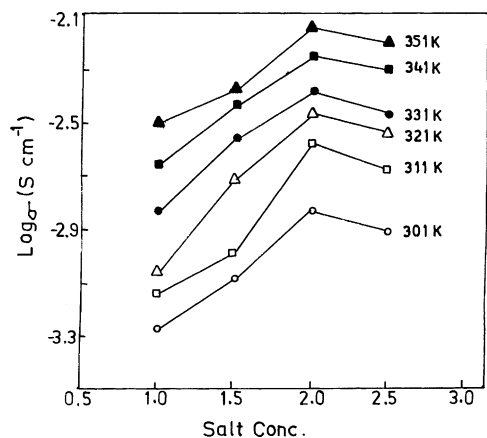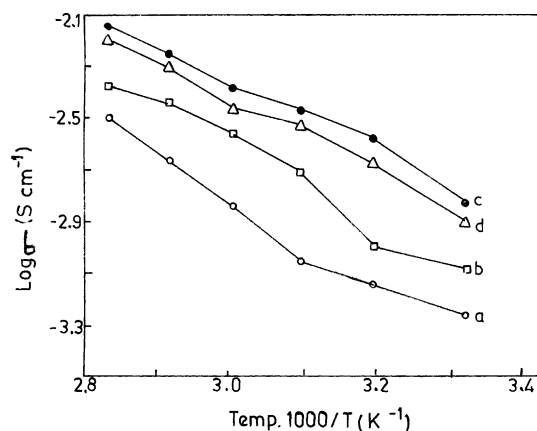

Fig. 5. Arrhenius plot of micro-porous polymer electrolyte for different salt concentration.

electrolyte depends upon segmental motion of the polymer electrolyte [16].

3.5. Transference number

The transference number of the micro-porous polymer membrane soaked in different concentrations of LiClO$_4$ electrolyte solution is given in Table 3 and a representative dc-polarization curve of micro-porous polymer membrane soaked in 2 M LiClO$_4$ electrolyte solution is shown in Fig. 6. Its corresponding ac-impedance spectrum is obtained before and after dc-polarization measurements with an applied dc potential difference of 10 mV. It can be seen from the figure that the initial current (I_0) is 18.75 μA and steady state value (I_s) is 10.14 μA within about 1.47 h and its corresponding ac-impedance values such as R_b^0, R_b^s, R_i^0 and R_i^s are 17.26, 17.38,

Table 3
Transference number of micro-porous polymer membrane soaked in different concentrations of LiClO$_4$ electrolyte solution

Concentration	Transference number
1 M LiClO$_4$	0.412
2 M LiClO$_4$	0.478
2.5 M LiClO$_4$	0.534
3 M LiClO$_4$	0.502

Fig. 4. Dependence of ionic conductivity on salt concentration for micro-porous polymer electrolyte at room temperature.
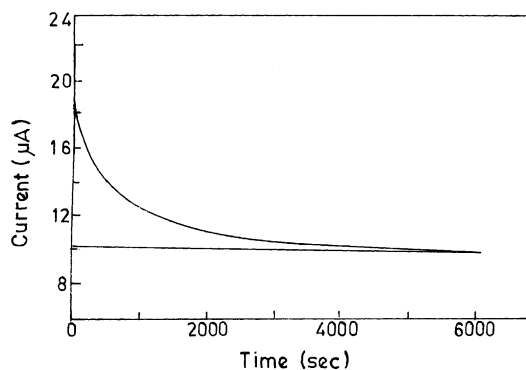

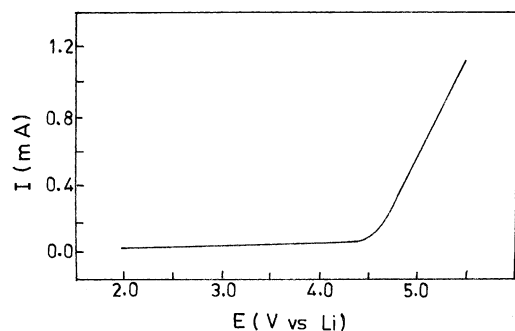Fig. 6. The dc-polarization curve of micro-porous polymer electrolyte.

Fig. 7. Linear sweep voltammogram curve of micro-porous polymer electrolyte.

29.31 and 55.19 Ω, respectively, which give the transference number (T_+) ca. 0.534. This reveals that no obvious change in the ac impedance spectra were observed before and after the dc polarization measurements. It confirms also that there will be no passive film formation between the polymer electrolyte and the lithium electrodes. It can be observed from the table that the transference number of micro-porous polymer electrolyte is also affected by lithium salt concentration.

3.6. Electrochemical stability

The electrochemical stability of micro-porous polymer electrolyte was studied by linear sweep voltammetry (LSV) and its corresponding voltammogram is shown in Fig. 7. It can be seen from the voltammogram that the decomposition voltage of the micro-porous polymer electrolyte is around 4.6 V versus Li/Li$^+$.

3.7. Cyclic voltammetry studies

Fig. 8 shows the cyclic voltammogram (CV) of the carbon/micro-porous polymer electrolyte/LiMn$_2$O$_4$ cell at room temperature. It can be seen from the cyclic voltammogram that the micro-porous polymer electrolyte has very good reversibility and electrochemical stability up to 4.6 V.
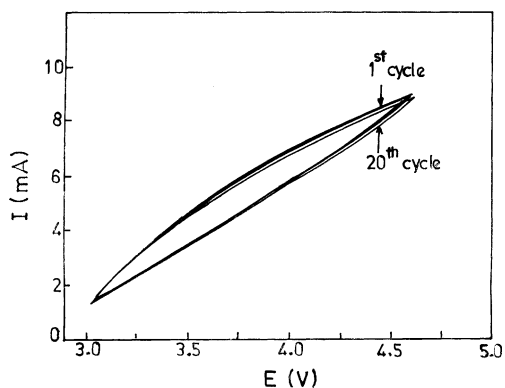

Fig. 8. Cyclic voltammogram curve of micro-porous polymer electrolyte film.

4. Conclusions

1. It is possible to prepare PVA based micro-porous polymer electrolyte by a simple preferential polymer dissolution process by extracting one of the polymers from the polymer blend film.
2. The maximum ionic conductivity of 1.5055×10^{-3} S cm^{-1} is observed when the micro-porous polymer membrane is soaked in 2 M LiClO$_4$ electrolyte solution.
3. The micro-porous polymer electrolyte has thermal stability up to 277.9 $^\circ$C.
4. The dependence of the ionic conductivity on temperature is non-linear on a logarithmic scale. It obeys the Arrhenius plot of conductivity and also it obeys the VTF relation.
5. The lithium transference number (T_+) of micro-porous gel polymer electrolyte is 0.534. However, the transference number of micro-porous polymer electrolyte is affected by Li-salt concentration.
6. The linear sweep and cyclic voltammogram studies confirm that the micro-porous polymer electrolyte has very good electrochemical stability up to 4.6 V besides very good reversibility.

Acknowledgement

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